

MERCURY OXIDATION IN CATALYSTS USED FOR SELECTIVE REDUCTION OF NO_x (SCR) IN OXY-FUEL COMBUSTION

Nuria Fernández-Miranda, M. Antonia Lopez-Anton*, Mercedes Díaz-Somoano,
M. Rosa Martínez-Tarazona

Instituto Nacional del Carbón (CSIC), Francisco Pintado Fe, 26, 33011, Oviedo, Spain

*Corresponding author:

Phone: +34 985 119090

Fax: +34 985 297662

Email: marian@incar.csic.es

Abstract

Emissions of mercury (Hg) and their control are a well-known problem for conventional coal combustion power plants but they still represent a challenge for relatively new technologies such as the oxy-combustion. In oxy-fuel combustion systems it is important that Hg be in its oxidized form (Hg^{2+}) because in the form of elemental mercury (Hg^0), it can damage the CO_2 compression units. In conventional air combustion some catalysts used in selective catalytic reduction (SCR) of NO_x could also co-benefit Hg oxidation. This study evaluates the oxidation of Hg in the presence of several SCR catalysts under an oxy-combustion atmosphere focusing on the main differences with conventional air coal combustion. In the experimental conditions of this study, a higher mercury oxidation was observed in the CO_2 -enriched atmosphere due to the fact that in this atmosphere the conversion of NO_x was lower, which resulted in a higher concentration of NO and NO_2 free to homogeneously oxidize mercury. In oxy-combustion conditions the high amount of CO_2 and H_2O present may block the active sites for mercury adsorption. Moreover, the differences between the active sites of catalysts based on V/W/ TiO_2 and Fe/Zelite with/without Mn as doping agent were eclipsed by the effect of the flue gas composition

Keywords: mercury; catalysts; oxy-combustion

1. Introduction

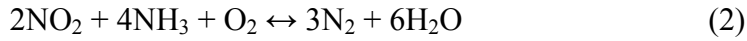
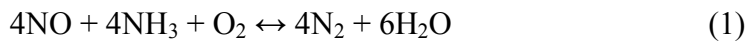
During the last decade, oxy-fired coal power plants have emerged as a promising technology for CO₂ capture. In oxy-combustion plants, coal is burned with a mixture of O₂ and recirculated flue gas, instead of air. This results in a flue gas stream with a high concentration of CO₂, suitable for purification, compression and storage. Despite the significant amount of fundamental and experimental research carried out on the oxy-combustion process [1-2], some uncertainties, such as the behavior of mercury and its control, still remain unsolved. Under oxy-fuel conditions higher Hg concentrations than in air-firing are to be expected [3-4]. High concentrations of mercury are a matter of concern not only because they are a danger to the environment but also because they cause technological problems as Hg can corrode the Al-alloys in the CO₂ compression units [5-6].

During combustion, mercury present in coal evaporates as elemental mercury (Hg⁰), but as the flue gas cools, it is partially transformed into oxidized species (Hg²⁺). The distribution, speciation and capture of Hg in a power plant depend on its content in the coal, the combustion conditions, halogen and sulfur species in the gas stream, unburned particles in fly ashes, etc. It is well known that Hg²⁺ can be retained in the flue gas desulphurization (FGD) units and particulate control systems and that Hg⁰ is more difficult to remove due to its insolubility in water and high volatility. Hg speciation and capture in oxy-fuel conditions may differ from coal combustion with air due to the increase in H₂O, HCl, SO_x and Hg concentrations in the flue gas and the change in NO_x concentrations caused by the absence of air-borne N₂ in oxy-combustion mode [7-8]. The presence of H₂O, HCl, NO_x and SO_x in the gas may improve the homogeneous oxidation of Hg depending on their relative proportions and concentrations [9]. The emissions control units installed in power stations are also a very important factor in

controlling Hg. FGD units, filters and selective catalytic reduction (SCR), installed for the control of SO_x, particulate matter and NO_x, respectively [10-11], may play an important role in mercury behaviour and capture.

This study is focused on evaluating the influence of some of the catalysts commonly used for SCR on Hg behavior in oxy-fuel combustion conditions.

The goal of SCR technology [12] is to reduce NO_x to nitrogen and water by injecting NH₃ according to the following reactions:



The reaction occurs over a catalyst, usually at 300-400°C. A co-benefit of SCR implementation is that it is also effective for oxidizing Hg⁰ to Hg²⁺ [13-14] favoring its retention in fly ashes and FGD systems, and in the case of the oxy-combustion, avoiding the corrosion caused by Hg⁰ in the compression units. A wide range of SCR catalysts are available. Most of them are prepared by using ceramic materials as supports, such as TiO₂, Fe₂O₃, Al₂O₃ or zeolite, and active catalytic components such as oxides of base metals (such as V, Cr, Mn, Co, W and Mo) or noble metals (Pt, Pd) [15]. There is a wide body of research focused on improving the activity of the catalyst [16-17], but there is a lack of knowledge on the behavior of SCR for emerging applications such as oxy-combustion [18-19]. An increase in the CO₂ concentration is not considered to have any effect on the behavior of the catalyst. However, an increase in SO₂ and SO₃ concentration in the flue gas of oxy-combustion [10, 20-22] can undermine the performance of the catalyst. SO₃ is known to form a sticky and corrosive ammonium bisulfate when NH₃ is added [23-24] and therefore, severe clogging of the catalyst can be expected. In a similar way, water vapor can contribute to reducing the number of available active sites on the surface of the catalyst [17]. Changes in the flue gas

composition and the effectiveness of the SCR system can modify the speciation of mercury [25], thereby affecting mercury retention during the oxy-combustion process. Wang et al. [11] evaluated the efficiency of a V_2O_5 - WO_3 / TiO_2 catalyst for Hg^0 removal in a CO_2 -enriched gas containing different concentrations of O_2 , CO_2 , NO and NH_3 . They recorded a high level of removal at 250-350°C for both Hg^0 and NO , attributing the removal of Hg^0 mainly to Hg oxidation. The degree of Hg oxidation throughout the SCR unit can also vary in the presence of other gases such as SO_x , HCl and H_2O . Mitsui et al [3] found that in a oxy-fuel combustion atmosphere, Hg oxidation throughout the SCR increased as the incoming HCl concentration increased, although the effect of HCl was similar to that of HCl in air combustion. Zhuang et al. [26] also analyzed the individual effects of HCl , SO_2 and SO_3 and concluded that sulfur species compete with HCl for adsorption sites on the SCR catalyst surface, reducing its capacity for Hg oxidation. Although the results described help in predicting the behavior of Hg in a SCR catalyst, more studies are necessary in order to confirm whether Hg oxidation takes place across a SCR unit in oxy-combustion conditions where not only CO_2 but also H_2O is present in high concentrations, and to reveal possible differences with an air combustion system.

The objective of the present work is to evaluate the oxidation and possible capture of Hg by SCR catalysts ($V/W/TiO_2$ and Fe /Zeolite) under a simulated flue gas of oxy-combustion where all the main possible gases are present (CO_2 , SO_x , HCl , O_2 , NO_x , H_2O , NH_3 and N_2).

2. Experimental part

2.1 Catalysts

The SCR catalysts were prepared by the Johnson Matthey technology center using an impregnation method in which the active SCR base metal component (Fe, V and W) was first impregnated on a powder support (TiO₂ and Zeolite) and then dried and calcined at 500°C. The powder catalysts were also aged hydrothermally at 550°C for 48hrs to simulate a de-greening phase or to partially age the catalysts. The effect of a separate mercury oxidation component on the powder-impregnated SCR catalysts was investigated by doping the standard SCR catalyst samples with manganese (Mn). The samples were characterized by different methods including surface area and porosity, XPS, XRD, H₂ TPR, NH₃ TPD and RAMAN spectroscopy. The results obtained have been published in the RFCR-CT-2007-00007 project report [27].

2.2 Experimental device

The capacity of the catalysts for NO_x reduction and Hg retention and oxidation was evaluated in the experimental laboratory scale device illustrated in Figure 1 (A) and Figure 1 (B), respectively. The device consists of: (1) a gas blending station equipped with mass flow controllers for preparing the different gas compositions (Table 1) focusing on the gas composition that simulates a typical oxy-combustion atmosphere (64% CO₂, 20% N₂, 12% H₂O, 4% O₂, 1000 ppm SO₂, 600 ppm NO, 100 ppm NO₂ and 25 ppm HCl); (2) a glass reactor (length, 500 mm; diameter, 25 mm) where the catalyst bed is situated. The bed was prepared by mixing 0.08 g of catalyst with 0.40 g of sand in order to avoid an excess of pressure in the system. The sand was previously tested showing not mercury retention and oxidation. The reactor was kept at 350°C. The total volume of flow gases that passed through the catalyst bed was 0.5 L·min⁻¹; (3) a TESTO 350 Gas Analyzer to evaluate the reduction of NO_x (Figure 1 (A)); (4) a calibrated permeation tube (VICI Metronic) placed inside a glass “U” tube immersed in a water

bath to obtain $100 \mu\text{g m}^{-3}$ of Hg^0 in gas phase and; (5) a continuous mercury analyzer (VM-3000) that monitored the signal of Hg^0 at the outlet of the reactor (Figure 1 (B)). The Hg^{2+} was captured by an ion exchanger resin (Dowex 1x8), suitable for the selective capture of Hg^{2+} species [28]. The resin was conditioned with a solution of $\text{HCl:H}_2\text{O}$ (1:1) at 90°C for 30 minutes and then filtered and dried. The resin was placed prior to the Hg^0 continuous analyzer in such a way that the total mercury concentration was balanced. The Hg^{2+} in the resin and in the condensed water at the end of the experiments and the mercury retained in the catalyst were measured using an automatic mercury analyzer (AMA 254).

3. Results and discussion

3.1 Characterization and activity of the catalysts

A summary of the most important conclusions from the characterization of the catalysts studied (V/W/TiO_2 , Mn-V/W/TiO_2 , Fe/Zelite and Mn-Fe/Zelite) has already been provided in a previous work [27]. Its findings that may help to interpret the results of the present study are the following: (i) When the SCR catalysts were doped with Mn (5-10 wt%) the specific surface area decreased, indicating that impregnation with metal species may have blocked or restricted access to the porous sites and (ii) analysis by XPS showed that the concentration of Mn on the surface of the Fe/Zelite support was lower than on the V/W/TiO_2 catalysts, suggesting that the shielding effect was greater or that more dopants were being exchanged inside the bulk of the Fe/Zelite material. The characteristics of the catalyst doped with Mn are mentioned here because this metal was added to improve Hg interactions.

In Project RFCR-CT-2007-00007 [27] the catalytic activity of the SCR catalysts in the conversion of NO_x and NH_3 to $\text{N}_2 + \text{H}_2\text{O}$ was also investigated. In that study, the

tests were carried out in conditions of 200 ppm NO_x, 200 ppm NH₃, 12% O₂, 4.5% CO₂, 4.5% H₂O, 200 ppm CO, 100 ppm C₃H₆, 20 ppm SO₂ and a N₂ balance. It was found that the selective catalytic reduction performances of the fresh zeolite and V/W/TiO₂ catalysts were very similar (~95% NO_x conversion). However, the Fe/zeolite had reduced SCR activity (~55%) after being doped with Mn. This may have been due to blockage of active sites and/or the exchange of metal ions which reduces the acidity of the catalysts. In the case of the V/W/TiO₂ catalysts the addition of Mn had little, to no effect, on the catalytic activity as the active sites were of a different nature to those of zeolites. As expected the catalytic activity decreased after ageing [27].

In light of the above results, the Hg behavior across the V/W/TiO₂ and Fe/Zeolite catalysts in an oxy-combustion atmosphere was evaluated using the experimental device described in Figure 1. Since the catalysts need to be effective for both the reduction of NO_x and the oxidation of Hg⁰, catalytic activity for NO_x reduction in these new conditions was assessed first (Figure 1 (A)). The experiments were carried out over a period of 12 h using the fresh catalysts with different gas compositions, as shown in Table 1. In this way the effect of the oxy-fuel gas composition can be evaluated and the differences between an oxy-combustion and an air combustion gas composition can be identified. The catalysts achieved NO_x reduction efficiencies ranging from 88 to 99% when no reactive gases were present, that is, in atmospheres that only contained NO₂, NO, NH₃ and O₂ (Figures 2-3) (Reactions 1 and 2). It is worth noting that, the percentages of NO and NO₂ conversion throughout the SCR catalyst decreased greatly in the oxy-combustion atmosphere 600 ppm NO, 100 ppm NO₂, 4% O₂, 64% CO₂, 20% N₂, 12% H₂O, 1000 ppm SO₂ and 25 ppm HCl plus 1000 ppm NH₃, (Figures 2-3). The capacity of the catalysts to convert NO_x was also lower in the atmosphere simulating conventional coal combustion with air. The explanation for this

low reactivity must be sought in the reactive gases. The deactivating effect of SO_2 on SCR catalysts, mainly in those supported on zeolite, is well known [17, 24], but it is not the only factor responsible for the deactivation of the catalyst. In fact, the reduction of NO_x was lower in the oxy-combustion atmosphere than in the air combustion atmosphere (Figures 2-3), whereas the SO_2 concentration and also the concentration of HCl were the same in both atmospheres. It appears that the different concentrations of CO_2 and H_2O also influence the reduction of NO_x . CO_2 and H_2O are present in oxy-fuel combustion in concentrations that are very different to those of air combustion. To establish why the reduction of NO_x decreased in oxy-combustion conditions to a greater extent than under air combustion (Figures 2-3), a series of experiments was carried out in which the concentration of H_2O was varied from 6 to 12%, while the CO_2 content was kept at 35%. The percentage of NO_x reduction was similar in all cases. However, when the experiments were conducted in an atmosphere with 16 and 64% CO_2 but without H_2O , the activity of the catalyst was lower in the atmosphere with the higher CO_2 concentration. It must be borne in mind that the diffusivity of NO_x may be different in an atmosphere enriched in CO_2 to what it is in N_2 [29]. In fact, according to a simplified equation of Fuller et al. [30] the coefficients of diffusivity for NO and NO_2 in an atmosphere enriched in CO_2 in the experimental conditions of this study are 0.667 and $0.658 \text{ cm}^2 \text{ s}^{-1}$, respectively, whereas in an atmosphere enriched in N_2 they are 1.015 and $0.831 \text{ cm}^2 \text{ s}^{-1}$, respectively. The conversion of NO_x is a mass transfer process which will be more limited in a CO_2 than in a N_2 atmosphere. Also to be taken into account is the possibility that CO_2 blocks, or competes for, the active sites of the catalysts, contributing, together with the acid gases, to a decrease in the efficiency of NO_x conversion. H_2O , on the other hand, although it may also contribute to the destruction

of the active sites of the catalyst, is not such a critical component because it is already being produced by the SCR reactions (Reactions 1-2).

3.2 Mercury behavior in the presence of the catalysts

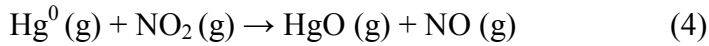
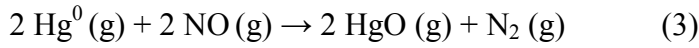
To evaluate the behavior of mercury in the presence of the catalysts, experiments were carried out in a simulated oxy-combustion flue gas and under an air coal combustion atmosphere. The mercury conversion rate with SCR depends on factors such as the temperature, acid gas composition and ammonia dosing rate [31]. The effect of these parameters has been previously evaluated in the Project RFCR-CT-2007-00007 [27]. In general, it can be inferred that i) when the temperature is increased, the oxidation of mercury decreases, ii) HCl has a beneficial effect on mercury oxidation iii) when the SO₂ concentration is increased slightly, mercury oxidation may be favored due to the higher acid load of the catalyst, making the catalysts more active for mercury oxidation and iv) a high concentration of ammonia can overload the catalysts' active sites and reduce the rate of mercury conversion. The task now is to assess the role of CO₂ and H₂O in the oxidation of mercury in the presence of the catalysts.

Figures 4-5 show the percentages of i) mercury (Hg⁰+Hg²⁺) retained in the catalysts (i.e., Hg_p), ii) the oxidized mercury in gas phase (Hg²⁺), resulting from homogeneous oxidation (gas-gas interaction) and heterogeneous oxidation (gas-catalytic interaction), and iii) the elemental mercury that was not retained in the sorbent (Hg⁰). The Hg²⁺ at the outlet of the reactor was determined by capturing it in an ion exchanger resin suitable for the selective extraction of Hg²⁺ species [28]. A resin bed was placed after the reactor in each mercury experiment which was then directly analyzed by means of AMA. The Hg²⁺ from homogeneous oxidation is the result of an analysis of the resin without the catalyst, whereas the Hg²⁺ from heterogeneous oxidation is the amount of

Hg^{2+} retained in the resin after the reactor with the catalyst. $15\pm 3\%$ of the Hg^{2+} was produced by homogeneous oxidation in both the simulated oxy-combustion and air combustion atmospheres (dotted line in Figures 4-5). The oxidation of Hg increased significantly in the presence of the V/W/TiO₂ and Fe/Zeolite catalysts in both atmospheres. However, in the oxy-combustion atmosphere the oxidation was higher (~80%) and mercury retention was negligible (Figure 4).

Apart from the mercury oxidation reactions, the possibility that mercury might be retained in the catalyst also needs be considered. The highest percentage of mercury retained in the sorbent (~20%), represented as Hgp, was achieved by V/W/TiO₂ in the conventional air coal combustion atmosphere (Figure 5). Wang et al. [11] proposed several reactions to explain mercury retention via mercury oxidation involving V₂O₅, O₂ and CO₂. However, in the present study, the catalyst-gas contact time was less than 1 second, implying that kinetic limitations in the reaction between Hg and V₂O₅ must be the cause of the low level of mercury removal, to the point where it was almost zero in oxy-fuel conditions. In the air combustion atmosphere differences became apparent when the catalyst was doped with Mn. The presence of Mn increased the oxidation of Hg but led to a decrease in mercury retention capacity. This was not altogether unexpected because the previous results obtained from the characterization of these catalysts [27] indicated a loss of BET surface area which would result in a decrease in mercury capture on the solid. It is to be noted that the distribution of mercury species was similar with either catalyst in the oxy-combustion atmosphere (Figure 4). It can be inferred, therefore, that the differences in the characteristics of the catalysts were eclipsed by the effect of the flue gas composition. In the oxy-combustion atmosphere Hg^{2+} was the main mercury species. A slightly lower NO_x conversion was observed in the oxy-combustion atmosphere than in the conventional air combustion atmosphere

(Figures 2-3). The lower NO_x conversion leaves more NH₃ free making it more difficult for the catalyst to oxidize the mercury [32-33]. However, the effect of NH₃ depends, among other factors, on the space velocity [32], the effect of NH₃ being low at a low space velocity (1.38 s⁻¹) [32]. In the present study the space velocity was <0.1 s⁻¹. Therefore, the higher Hg oxidation observed in the oxy-combustion than in the air combustion atmosphere (Figures 4-5) is a consequence of the fact that the lower NO_x conversion results in a higher concentration of NO_x in the flue gas which, in turn, favors Hg homogeneous oxidation through Reactions 3 and 4 [9].



Moreover, the large proportion of CO₂ might also be competing for the same adsorption sites as the mercury which would explain why the catalyst retained almost no mercury in the oxy-combustion atmosphere.

4. Conclusions

A comparison of the capacities of SCR catalysts to oxidize and capture mercury in simulated atmospheres of air and oxy-combustion showed that a greater level of mercury oxidation was produced in the enriched-CO₂ atmosphere in the experimental conditions of this study. The results suggest that in an atmosphere enriched in CO₂ the conversion of NO_x is lower than in an atmosphere enriched in N₂, leaving more NO and NO₂ free to homogeneously oxidize mercury. Although kinetic limitations must also be taken into consideration, it can be inferred that in oxy-combustion conditions the presence of a large amount of CO₂ decreases the number of active sites available for mercury adsorption. In these conditions, the different natures of the active sites of

catalysts based on V/W/TiO₂ or Fe/Zeolite with/without Mn are eclipsed by the effect of the flue gas composition.

Acknowledgments

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References

- [1] L. Zheng, Oxy-Fuel Combustion for Power Generation and Carbon Dioxide (CO₂) Capture, Woodhead Publishing Series in Energy, ISBN: 978-1-84569-671-9, 2011, 400 pp.
- [2] G. Scheffknecht, L. Al-Makhadmeh, U. Schnell, J. Maier, Oxy-fuel coal combustion-A review of the current state-of-the-art, Int. J. Greenhouse Gas Control 5 (2011) 16-35.
- [3] Y. Mitsui, N. Imada, H. Kikkawa, A. Katagawa, Study of Hg and SO₃ behavior in flue gas of oxy-fuel combustion system, Int. J. Greenhouse Gas Control 5 (2011) 143-150.
- [4] B. Roy, W.L. Choo, S. Bhattacharya, Prediction of distribution of trace elements under oxy-fuel combustion condition using Victorian brown coals, Fuel 114 (2013) 135-142.
- [5] J.B. Bessone, The activation of aluminium by mercury ions in non-aggressive media, Corros. Sci. 48 (2006) 4243-4256.

- [6] S.O. Santos, IEA Greenhouse. Gas R&D Programme Cheltenham, MEC7 Workshop DLCS, Strathclyde University, United Kingdom, 2010.
- [7] J.H. Pavlish, L.L. Hamre, Y. Zhuang, Mercury control technologies for coal combustion and gasification systems, *Fuel* 89 (2010) 838-847.
- [8] R. Spörl, Flue Gas Impurities, their impact and control under oxy-fuel conditions, 5th Oxy-Fuel Capacity Building Course, Ponferrada, Spain 9th, 2013.
- [9] N. Fernández-Miranda, M.A. Lopez-Anton, M. Díaz-Somoano, M.R. Martinez-Tarazona, Effect of oxy-combustion flue gas on mercury oxidation, *Environ. Sci. Technol.* 48 (2014) 7164-7170.
- [10] R. Spörl, J. Maier, L. Belo, K. Shah, R. Stanger, T. Wall, G. Scheffknecht, Mercury and SO₃ emissions in oxy-fuel combustion, *Energy Procedia* 63 (2014) 386-402.
- [11] F. Wang, G. Li, B. Shen, Y. Wang, C. He, Mercury removal over the vanadia-titania catalyst in CO₂-enriched conditions, *Chem. Eng. J.* 263 (2015) 356-363.
- [12] F. Normann, K. Andersson, B. Leckner, F. Johnsson, Emission control of nitrogen oxides in the oxy-fuel process, *Prog. Energ. Combust.* 35 (2009) 385-397.
- [13] H. Gutberlet, A. Schluten, A. Lienta, SCR impacts on mercury emissions on coal-fired boilers, EPRI's SCR Workshop, Memphis, Tennessee, 2000.
- [14] J. Kilgroe, C. Senior, Fundamental Science and Engineering of Mercury Control in Coal-fired Power Plants, Air Quality IV Conference, Arlington, VA, 2003.
- [15] D.W. Lee, B.R. Yoo, Advanced metal oxide (supported) catalysts: Synthesis and applications, *J. Ind. Eng. Chem.* 20 (2014) 3947-3959.
- [16] L. Qu, C. Li, G. Zeng, M. Zhang, M. Fu, J. Ma, F. Zhan, D. Luo, Support modification for improving the performance of MnO_x-CeO_y/γ-Al₂O₃ in selective catalytic reduction of NO by NH₃, *Chem. Eng. J.* 242 (2014) 76-85.

- [17] J. Li, H. Chang, L. Ma, J. Hao, R.T. Yang, Low-temperature selective catalytic reduction of NO_x with NH₃ over metal oxide and zeolite catalysts-A review, *Catal. Today* 175 (2011) 147-156.
- [18] X. Cheng, X.T. Bi, A review of recent advances in selective catalytic NO_x reduction reactor technologies, *Particuology* 16 (2014) 1-18.
- [19] M.B. Toftegaard, J. Brix, P.A. Jensen, P. Glarborg, A.D. Jensen, Oxy-fuel combustion of solid fuels, *Prog. Energ. Combust.* 36 (2010) 581-625.
- [20] D. Fleig, K. Andersson, F. Normann, F. Johnsson, SO₃ formation under oxy-fuel combustion conditions, *Ind. Eng. Chem. Res.* 50 (2011) 8505-8514.
- [21] J. Ahn, R. Okerlund, A. Fry, E.G. Eddings, Sulfur trioxide formation during oxy-coal combustion. *Int. J. Greenhouse Gas Control* 5 (2011) 127-135.
- [22] J.R. Kenney, M.M. Clrak, A.A. Levasseur, S.G. Kang, SO₃ emissions from a tangentially fired pilot scale boiler operating under oxy-combustion conditions, IEA GHG Special Workshop on Oxyfuel Combustion, London, UK, January 26th, 2011.
- [23] M. Klostermann, Efficiency increase of the oxyfuel process by waste heat recovery considering the flue gas treatment, In: 3rd workshop of the IEA GHG international oxy-combustion network. Yokohama, Japan, March 5-6, 2008.
- [24] Z. Sheng, Y. Hu, J. Xue, X. Wang, W. Liao, SO₂ poisoning and regeneration of Mn-Ce/TiO₂ catalyst for low temperature NO_x reduction with NH₃, *J. Rare Earth.* 30 (2012) 676-682.
- [25] L. Hailong, L. Ying, W. Chang-Yu, Z. Junying, Oxidation and capture of elemental mercury over SiO₂-TiO₂-V₂O₅ catalysts in simulated low-rank coal combustion flue gas, *Chem. Eng. J* 169 (2011) 186-193.

- [26] Y. Zhuang, J. Laumb, R. Liggett, M. Holmes, J.H. Pavlish, Impacts of acid gases on mercury oxidation across SCR catalyst, *Fuel Process. Technol.* 88 (2007) 929-934.
- [27] Report *High Capacity Sorbents and Optimisation of Existing Pollution Control Technology for Mercury Capture in Industrial Combustion Systems*. Project RFCR-CT-2007-00007; p44, 2011. Available in: http://cordis.europa.eu/project/rcn/87193_en.html
- [28] A. Fuente-Cuesta, M. Díaz-Somoano, M.A. López-Antón, M.R. Martínez-Tarazona, Oxidised mercury determination from combustion gases using an ionic exchanger, *Fuel* 122 (2014) 218-222.
- [29] M.J. Tang, R.A. Cox, M. Kalberer, Compilation and evaluation of gas phase diffusion coefficients of reactive trace gases in the atmosphere: volume 1. Inorganic compounds, *Atmos. Chem. Phys.* 14 (2014) 9233–9247.
- [30] E.N. Fuller, P.D. Schettler, J.C. Giddings, New method for prediction of binary gas-phase diffusion coefficients, *Ind. Eng. Chem.* 58 (1966) 18–27.
- [31] M. Rallo, B. Heidel, K. Brechtel, M.M. Maroto-Valer, Effect of SCR operation variables on mercury speciation, *Chem. Eng. J.* 198-199 (2012) 87-94.
- [32] C. Richardson, T. Machalek, S. Miller, C. Dene, R. Chang, Effect of NO_x Control Processes on Mercury Speciation in Utility Flue Gas, *J. Air Waste Manage. Assoc.* 52 (2002) 941-947.
- [33] Y. Gao, Z. Zhang, J. Wu, L. Duan, A. Umar, L. Sun, Z. Guo, Q. Wang, A Critical Review on the Heterogeneous Catalytic Oxidation of Elemental Mercury in Flue Gases, *Environ. Sci. Technol.* 47 (2013) 10813–10823.

Figure captions

Figure 1. Schematic diagram of the experimental device for (A) NO_x reduction and (B) Hg retention and oxidation.

Figure 2. Performance of the SCR catalysts at 350°C on NO conversion in different flue gas compositions.

Figure 3. Performance of the SCR catalysts at 350°C on NO₂ conversion in different flue gas compositions.

Figure 4. Percentages of mercury retained in the catalysts (H_{gp}), oxidized mercury (Hg²⁺) and elemental mercury (Hg⁰) in an oxy-combustion atmosphere.

Figure 5. Percentages of mercury retained in the catalysts (H_{gp}), oxidized mercury (Hg²⁺) and elemental mercury (Hg⁰) in an air coal combustion atmosphere.

Table 1. The composition of the main atmospheres evaluated

	Oxy-combustion	Air-combustion	NO _x +NH ₃ +O ₂
CO ₂	64%	20%	-----
N ₂	20%	70%	balance
H ₂ O	12%	6%	-----
O ₂	4%	4%	4%
SO ₂	1000 ppm	1000 ppm	----
NO	600 ppm	600 ppm	600 ppm
NO ₂	100 ppm	100 ppm	100 ppm
HCl	25 ppm	25 ppm	-----
NH ₃	1000 ppm	1000 ppm	1000 ppm

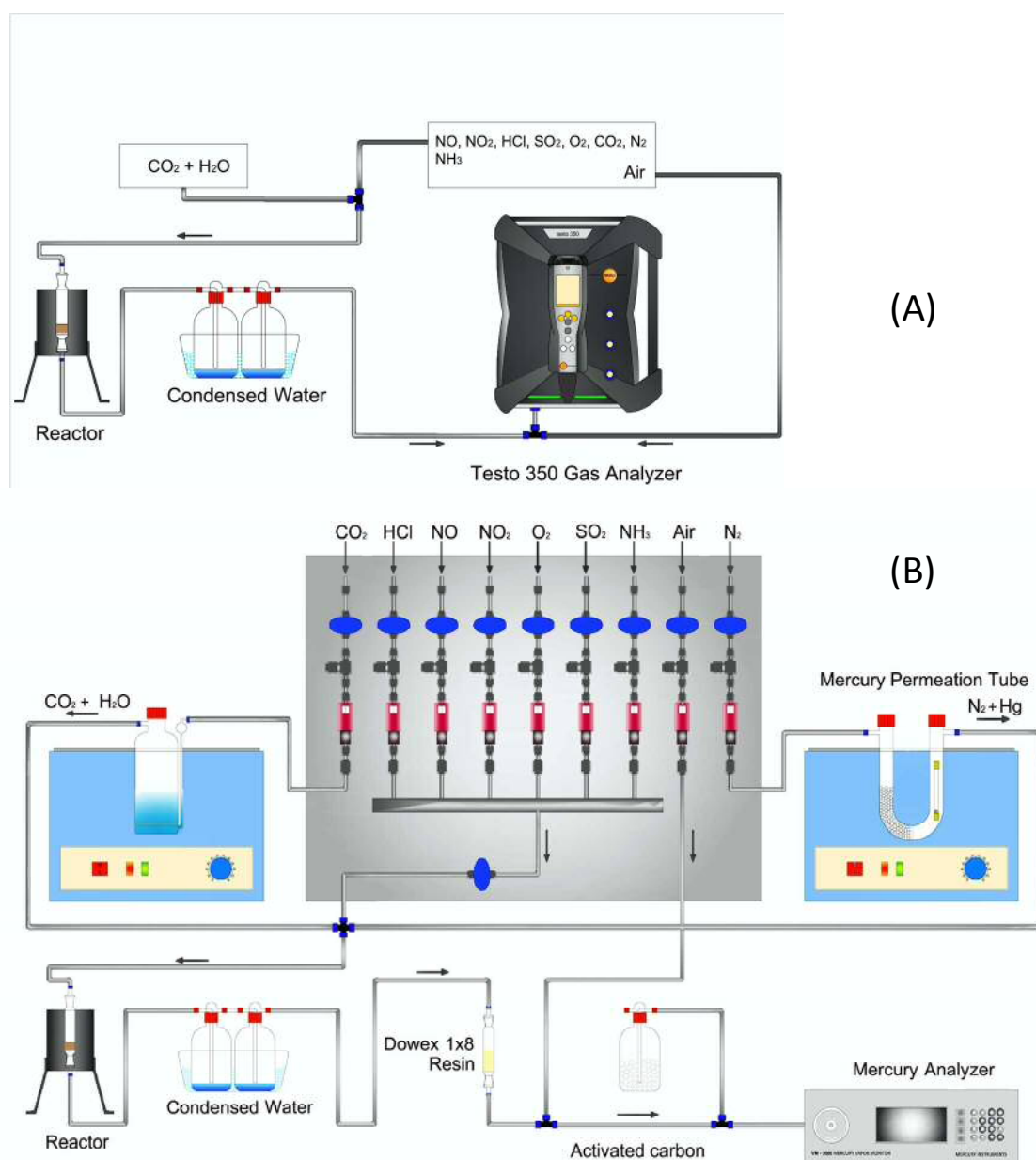


Figure 1

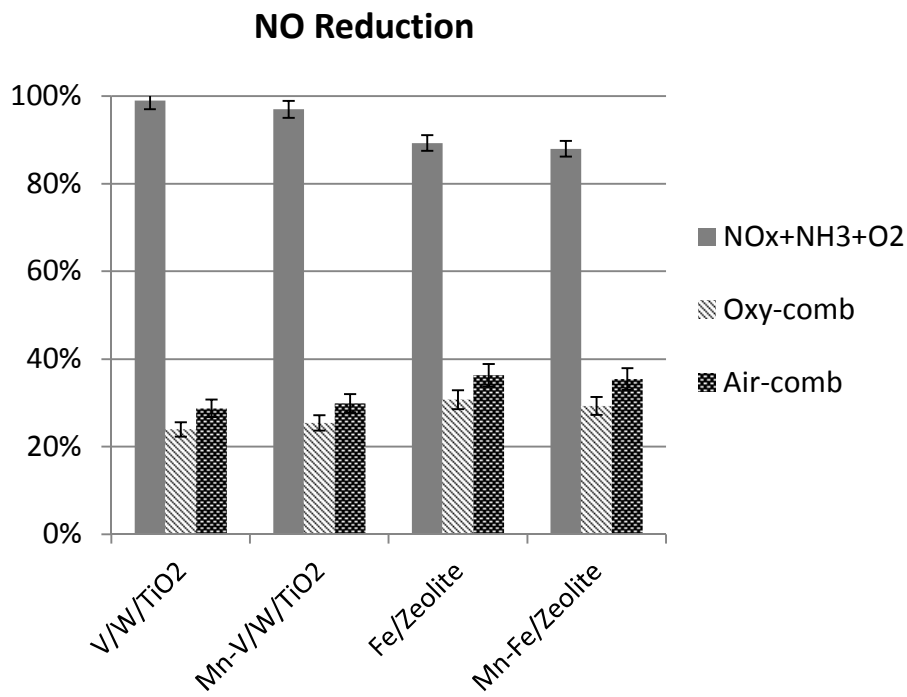


Figure 2

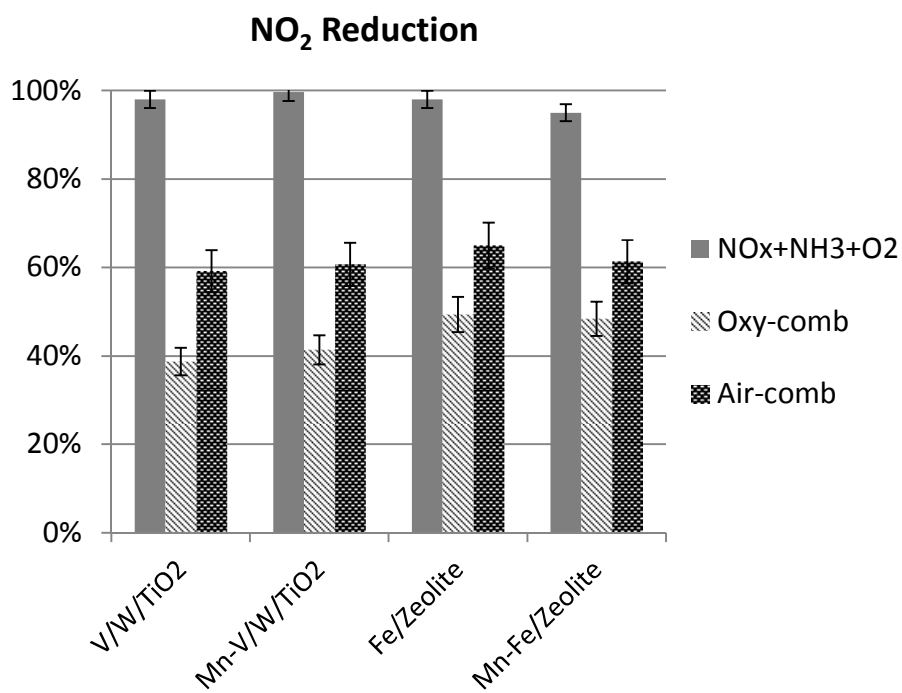


Figure 3

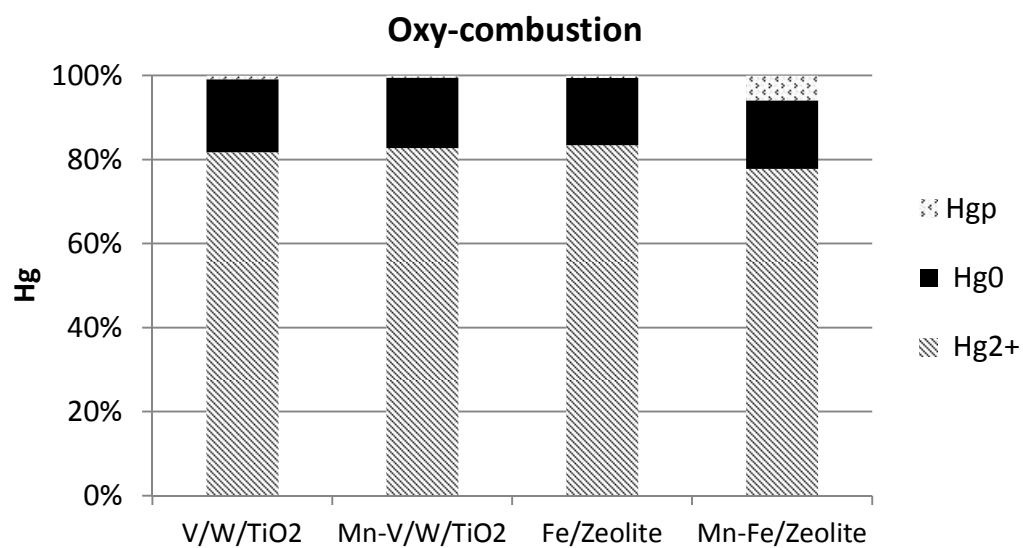


Figure 4

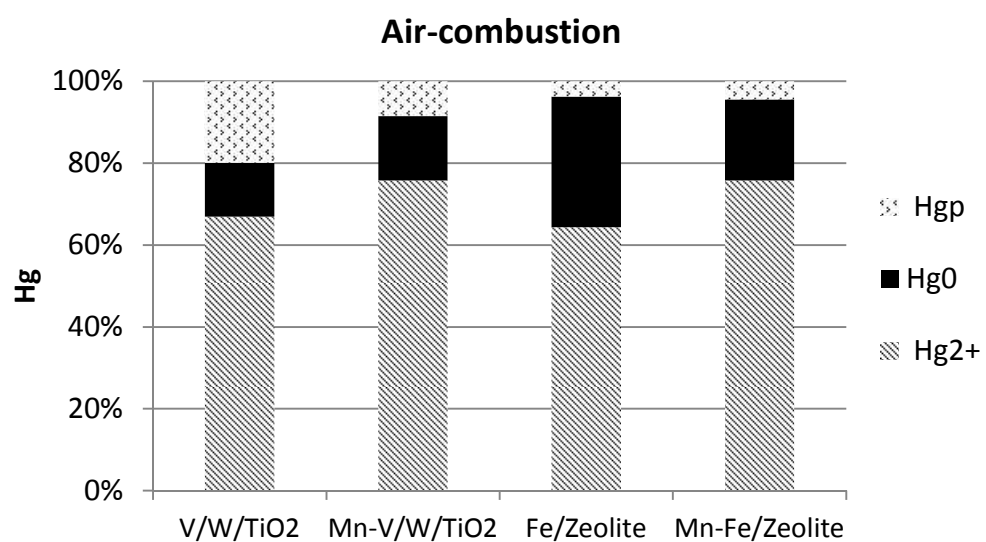


Figure 5